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(54) Coated glazing material

(57) Glazing material bears a pyrolytically-formed light-transmitting solar radiation screening metal oxide coating. In order to promote abrasion resistance in a coating which has an acceptable tint in reflection due to interference effects, at least 95% by weight of the metal ions in the coating consist of tin and titanium, and the relative proportions of tin and titanium ions in the coating are such as to impart to the coating a refractive index which is not greater than 2.2.

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SPECIFICATION

Coated glazing material

5 This invention relates to glazing material bearing a pyrolytically formed, light transmitting, solar radiation screening, metal oxide coating. 5

The use of window glass bearing a solar radiation screening coating is well known for glazing buildings in order to reduce the solar heat gain of the building, especially during hot sunny weather, in order that the temperature within the building may easily be maintained at a level 10 which for example is comfortable for occupants of the building and can be tolerated by any computers or other temperature sensitive electronic equipment which may be housed within the building. 10

By way of example, it is known from European Patent Specification No. EP 0 075 516 A1 to provide glass with a solar radiation screening coating of titanium dioxide deposited in an amount 15 of the order of 140mg/m², which correspond to a thickness of about 35nm. Known window glass with a coating of titanium dioxide 35 to 40 nm thick provides an effective screen for solar radiation and gives a metallic tint in reflection due to interference effects. Commercially, it is extremely important that such a coating should give rise to a tint in reflection which is neutral or otherwise aesthetically acceptable. Unfortunately, known coatings of titanium dioxide up to 20 40nm thick used for this purpose are too thin to have adequate abrasion resistance so that the product has an insufficient useful life. It would be possible to impart additional abrasion resistance to the coating by making it thicker. For example it has been found that titanium dioxide coatings having a thickness in the range 50nm and 60nm can have a satisfactory abrasion resistance for the purposes in view. However increasing the thickness of such a coating 25 will have the effect of altering its tint in reflection, and a 50 nm to 60 nm titanium dioxide coating gives an unpleasant yellowish colour in reflection. 25

It is an object of the present invention to provide glazing material bearing a pyrolytically formed, light transmitting, solar radiation screening, metal oxide coating such that the colour of the coating, when viewed in reflection, can be varied in a manner which is not wholly 30 dependent on the thickness of the coating. 30

According to the present invention, there is provided glazing material bearing a pyrolytically formed, light transmitting, solar radiation screening, metal oxide coating, characterised in that at least 95% by weight of the metal ions in the coating consist of tin and titanium and in that the relative proportions of tin and titanium ions in the coating are such as to impart to the coating a 35 refractive index which is not greater than 2.2. 35

The refractive index of a thin pyrolytically formed titanium oxide coating is about 2.3. By the adoption of the present invention, the refractive index of the coating as a whole is reduced by the addition of sufficient tin ions, and accordingly, a coating according to the invention can be made to the same optical thickness as, but to a greater actual thickness than a coating of 40 substantially pure titanium dioxide. It will be appreciated that the abrasion resistance of such a coating is dependent on the nature and actual thickness of the coating, whereas any interference effects due to the coating will depend on its optical thickness. The optical thickness of a coating which governs its reflective properties is given by twice its actual thickness multiplied by its refractive index. Accordingly the present invention provides a means of enhancing the abrasion 45 resistance of a said coating while controlling its colour in reflection so that the resulting coating has better aging properties. Abrasion resistance of a coating according to the invention is enhanced as compared with a titanium dioxide coating of the same optical thickness, because the coating according to the invention has a greater actual thickness, and also because the addition of tin ions modifies the nature of the coating in a way which is beneficial for promoting 50 abrasion resistance. Thus it is possible to simulate a thin titanium dioxide coating, but with better aging properties. 50

The refractive index of a said coating can be measured by a classical ellipsometry technique as described in "Thin Film Phenomena", K.L. Chopra, McGraw Hill, 1969, pages 738 to 741, and references in this specification to specific values of refractive index are references to values 55 measured by that technique, the measurement being effected using sodium D light. 55

To test the abrasion resistance of a said coating, use can be made of an annular reciprocating rubber member having an internal diameter of 2cm and an external diameter of 6cm to give a rubbing surface area of 25cm² and formed by a felt pad on an annular metal member. The rubbing member is set in a weighted tube (weight of assembly: 1.7kg) sliding vertically in a 60 support. Constant contact is thereby ensured between the rubbing member and the sample. The hole through the annular metal member forms a reservoir for an aqueous suspension of crushed sand having a mean grain diameter of 0.1mm which is allowed to flow out between the felt pad and the coated glazing material being tested. The support carrying the rubbing member is reciprocated by a crank system, with an amplitude of 3cm at a frequency of 1Hz. After a certain 65 time, a pattern of wear is obtained formed by scratches very close together, with undestroyed 65

coating left between them, followed eventually by complete or substantially complete removal of the coating. Specific or comparative references in this specification to abrasion resistance, are references to abrasion resistance as measured by that test.

In the most preferred embodiments of the present invention, the relative proportions of tin and titanium ions in the coating are such as to impart to the coating a refractive index which is at least 1.9. This ensures that there will be a high degree of visible light reflection at the coating. 5

Advantageously, the relative proportions of tin and titanium ions in the coating are such as to impart to the coating a refractive index which is not greater than 2.15. This allows a correspondingly greater actual thickness for a given optical thickness of the coating. 10

Preferably, said coating comprises at least 30% tin and at least 30% titanium calculated as weight per cent of the respective dioxide in the coating. It has been found that this gives the best compromise between the solar radiation screening properties of the coating (which are largely due to the presence of titanium) and reduction in refractive index and increase in abrasion resistance (which is attributable to the presence of tin). To achieve the best abrasion resistance, it is preferred that said coating comprises at least 40% tin calculated as weight per cent of tin dioxide in the coating. 15

In the most preferred embodiments of the invention, the thickness of the coating and the relative proportions of tin and titanium ions in the coating are such as to give interference enhancement of visible light reflection within the wavelength range less than 500nm. In this way, the glazing material will exhibit a metallic tint when viewed by ordinary daylight in reflection from the coated side. 20

Advantageously, the coating is borne by sheet glass.

Such glass may be clear glass, or it may be opaque glass, for example for use as external cladding panels for buildings at floor levels. Embodiments of the invention in which the sheet glass is tinted glass, for example, bronze glass, have advantageous light absorbing properties. 25

Various preferred embodiments of the invention will now be described in greater detail in the following Examples.

30 TEST SAMPLE 30

A titanium dioxide coating 45nm thick can be formed on glass as described in Example 1 of British Patent Specification No 1 397 741 by pyrolysis of titanyl acetylacetonate. It has been found that when formed in that way, the titanium dioxide coating has a refractive index of 2.3, and thus an optical thickness in reflection of 207nm. When the abrasion resistance of this coating was tested, it was found that over at least the central region of the abraded area, the coating was substantially completely removed within 5 minutes. 35

EXAMPLE 1

An oxide coating comprising 40% tin and 60% titanium calculated as weight per cent of the respective dioxide in the coating was formed by pyrolysis on a hot glass substrate of a solution containing titanyl acetylacetonate and tin dibutyldiacetate. The resulting coating had a refractive index of 1.9, and was formed to a thickness of 55nm, so that it had the same optical thickness as the coating of the Test Sample. When the abrasion resistance of this coating was tested, after abrasion for 30 minutes, it was found that a few scratches were apparent in the coating when the coating was inspected through a microscope. 40 45

The coating exhibited a metallic tint in reflection.

In a variant of this Example the coating was formed on tinted glass to give a reduction in luminous transmission.

50 EXAMPLE 2 50

A 6mm thick ribbon of freshly formed hot clear float glass was conveyed through a coating station at a speed of 8.5 metres per minute. The atmosphere in the coating station had a mean temperature of about 300°C, and the ribbon entering that station had a mean temperature of about 600°C.

A coating precursor solution was made up as follows: 55

Tin dibutyldiacetate	6.7 kg
Titanium diacetylacetonatediisopropylate	12.5 kg
Dimethylformamide to	100 L

This solution was sprayed at a rate of 120 litres per hour to form a coating 42nm thick on the glass ribbon. 60

The calculated composition of the coating by weight was 47% tin dioxide and 53% titanium dioxide, and the coating had a refractive index of 1.9.

With light incident on the coated face of a sheet cut from this ribbon, the luminous 65

transmission of the sheet was 74.2% and the reflectivity of light from the coated face was 22.5%. The coating exhibited a metallic tint in reflection, and its abrasion resistance was similar to that specified in Example 1.

In a variant of this Example, the coating was formed on tinted glass to give a reduction in luminous transmission.

EXAMPLE 3

An 8mm thick ribbon of clear float glass was coated while hot by pyrolysis of a coating precursor solution made up as follows:

10	Tin dibutyldiacetate	9.3 kg	10
	Titanium diacetylacetonatediisopropylate	27.8 kg	
	Dimethylformamide to	100 L	

15 The solution was discharged against the ribbon at a rate of 87 litres per hour to form a coating 53nm thick containing 40% tin dioxide by weight. The refractive index of the coating was 2.1.

With light incident on the coated face of a sheet cut from this ribbon, the luminous transmission of the sheet was 66% and the reflectivity of light from the coated face was 28%.

20 The coating exhibited a metallic tint in reflection, and its abrasion resistance was similar to that specified in Example 1.

In a variant of this Example the coating was formed on tinted glass to give a reduction in luminous transmission.

25 EXAMPLE 4

A 6mm thick ribbon of freshly formed hot bronze float glass was conveyed through a coating station.

A coating precursor solution was made up as follows:

30	Tin dibutyldiacetate	13.2 kg	30
	Titanium diacetylacetonatediisopropylate	27.8 kg	
	Dimethylformamide to	100 L	

This solution was sprayed at a rate of 82 litres per hour to form a coating 50nm thick on the glass ribbon.

The calculated composition of the coating by weight was 42% tin dioxide and 58% titanium dioxide, and the coating had a refractive index of 2.1.

With light incident on the coated face of a sheet cut from this ribbon, the luminous transmission of the sheet was 39% and the reflectivity of light from the coated face was 24%.

40 The coating exhibited a metallic tint in reflection, and its abrasion resistance was similar to that specified in Example 1.

In a variant of any of the foregoing Examples, the coating precursor solution used contained additional ingredients so as to form in the coating a doping agent constituting up to 5% by weight of the metal ions in the coating, the relative proportions of tin and titanium dioxides

45 remaining as specified.

CLAIMS

1. Glazing material bearing a pyrolytically formed, light transmitting, solar radiation screening, metal oxide coating, characterised in that at least 95% by weight of the metal ions in the coating consist of tin and titanium and in that the relative proportions of tin and titanium ions in the coating are such as to impart to the coating a refractive index which is not greater than 2.2.

2. Glazing material according to claim 1, wherein the relative proportions of tin and titanium ions in the coating are such as to impart to the coating a refractive index which is at least 1.9.

3. Glazing material according to claim 1 or 2, wherein the relative proportions of tin and titanium ions in the coating are such as to impart to the coating a refractive index which is not greater than 2.15.

4. Glazing material according to any preceding claim, wherein said coating comprises at least 30% tin and at least 30% titanium calculated as weight per cent of the respective dioxide in the coating.

5. Glazing material according to claim 4, wherein said coating comprises at least 40% tin calculated as weight per cent of tin dioxide in the coating.

6. Glazing material according to any preceding claim, wherein the thickness of the coating and the relative proportions of tin and titanium ions in the coating are such as to give interference enhancement of visible light reflection within the wavelength range less than

65 500nm.

7. Glazing material according to any preceding claim, wherein the coating is borne by sheet glass.
8. Glazing material according to claim 7, wherein the sheet glass is tinted glass.

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